Highlights from Recent Literature

1 ANALYTICAL

1.1 Controlling Atomizer Surfaces in Electrothermal Atomic Absorption Spectrometry

Ascorbic acid pyrolysis has been used as a chemical modifier on kinetic parameters for atomic absorption signals for gold: the effect of the temperature and hold time of the ascorbic acid pyrolysis step was studied. S. Imai, K. Naniwa, E. Iwamoto, Y. Nishiyama and Y. Hayashi of the Faculty of Integrated Arts and Sciences, Department of Chemistry, The University of Tokushima, Japan, *J. Anal. At. Spectrom.,* 2001, **16**(4), 398-403, analysed the signal for gold, dispersed individually into micro-sized pores, using Arrhenius plots based on solid-phase kinetics. First order kinetics, corresponding to desorption of individually dispersed atoms, was the best possible fit for all the plots.

Using mass dependency of the absorbance-time profile characteristics and activation energy the kinetics were confirmed as first order. Increasing the temperature of pyrolysis of ascorbic acid to 1676 K decreased the activation energy (E_a) for desorption of the gold atoms from 325 ±11 kJ mol^{-1} to 108 ±10 kJ mol^{-1}. Below a pyrolysis temperature of 1676 K, the E_a value was nearly constant. The change in E_a with pyrolysis temperature, is discussed from the viewpoint of a change in the degree of interaction with the pore wall surface relating to a change in degree of the surface roughness.

2 CATALYSIS

2.1 Hydrodechlorination of CCl_2F_2 (CFC-12) over Pd/Au/SiO_2 Catalysts

M. Bonarowska, A. Malinowski, W. Juszczyk and Z. Karpinski of the Department of Catalysis on Metals, Institute of Physical Chemistry, Polish Academy of Sciences, Warsaw, Poland, *Appl. Catal., B,* 2001, **30**(1,2), 187-193, have prepared two series of well-mixed Pd-Au/SiO_2 catalysts using a direct redox method. These were evaluated in the reaction of CCl_2F_2 (CFC-12) hydrodechlorination. A moderate selectivity for CH_2F_2 exhibited by monometallic Pd/SiO_2 (*ca* 40%) is significantly increased, up to *ca* 95%, by the addition of gold. Proper Pd-Au alloying is essential to obtain such a selectivity enhancement. Poorly mixed Pd-Au/SiO_2 catalysts show the catalytic behaviour not very much different from that of Pd/SiO_2, producing a lot of methane. Changes in the apparent activation energy are also associated with the degree of Pd-Au alloying. After reaction, the Pd/SiO_2 and Pd-Au/SiO_2 catalysts contain dissolved carbon. Hydrogen treatment of carbonized Pd-Au catalysts removes this carbon. XRD study of the regenerated samples shows no change in the structure and composition of the Pd-Au phase, compared to freshly pre-reduced bimetallic SiO_2 catalysts.

2.2 ^{197}Au Mössbauer Study of Nano-Sized Gold Catalysts Supported on $Mg(OH)_2$ and TiO_2

Nano-sized gold catalysts supported on $Mg(OH)_2$ and TiO_2 were characterized by Y. Kobayashi, S. Nasu, S. Tsubota and M. Haruta, Research Reactor Institute, Kyoto University, Osaka, Japan, *Hyperfine Interact.,* 2000, **126**(1-4), 95-99, using ^{197}Au Mössbauer spectroscopy. ^{197}Au Mössbauer spectra recorded for Au/$Mg(OH)_2$ catalysts include one singlet with zero isomer shift and several doublets. One of the doublets shows an isomer shift that is typical of Au^{I}, and the other doublets arise from Au^{III}. The relative area of the Au^{I} component shows the maximum value for a specimen calcined at 523 K, and this sample also shows the highest catalytic activity.

2.3 Characteristics of Supported Gold Catalysts Prepared using a Spray Reaction Technique

Gold nanoparticle catalysts on titania supports were prepared using a spray reaction (SPR) technique. The structure of the spr-Au/TiO_2 catalysts was studied by SEM, TEM and XRD (L. Fan, N. Ichikuni, S. Shimazu and T. Uematsu, Center for Frontier Electronics and Photonics, Chiba University, Japan, *Stud. Surf. Sci. Catal.,* 2001, **132**(Proceedings of the International Conference on Colloid and Surface Science, 2000, 769-772). The effects of preparation conditions for the spray reaction, such as the solution concentration and the calcination temperature, on the surface characteristics are discussed. The spr-Au/TiO_2 catalysts calcined at high temperature gave a high turnover frequency (TOF) for carbon monoxide oxidation despite the limited active sites. The high catalytic activity was attributed to the extensive perimeter interface between gold and TiO_2 support particles, which enhanced a synergistic effect.

2.4 Deposition of Highly Dispersed Gold on Alumina Support

Au/Al_2O_3 catalysts, prepared using deposition precipitation (DP), using $AuCl_3$ as the source of gold, and chemical vapour deposition (CVD) using an organic gold complex as the precursor, were evaluated for CO oxidation activity at sub-ambient temperatures by Y.-J. Chen and C.-T. Yeh,

Department of Chemistry, National Tsinghua University, Hsinchu, Taiwan, *J. Catal.,* 2001, **200**(1), 59-68. The activity observed generally increased with their degree of gold dispersion as measured by transmission electron microscopy. Finely dispersed Au/Al_2O_3 catalysts (with d_{Au}<5 nm) were readily prepared using CVD, but Au/Al_2O_3 samples prepared using the traditional DP method contained many large gold crystallites (d_{Au} > 7 nm). They originated, during the impregnation step, from the occlusion of the gold complex solution in the pores of Al_2O_3. However, small gold particles (d_{Au} *ca* 3.5 nm) may be deposited on Al_2O_3 using a modified DP method involving prealkalinization of the Al_2O_3 surface. Furthermore, a mild hydrogen reduction is effective in eliminating the incubation period required for catalysts freshly prepared by the DP method. Characterization of the catalysts using TPR revealed that the function of reduction was to remove poisonous chloride ions from deposited gold crystallites.

2.5 Photon Emission from Individual Supported Gold Clusters: Thin Film versus Bulk Oxide

To examine the effects of different substrates (Al_2O_3/NiAl and TiO_2) on the electronic properties of single, selected gold particles N. Nilius, N. Ernst and H.-J. Freund, Department of Chemical Physics, Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, *Surf. Sci.,* 2001, **478**(1-2), L327-L332, have measured electron-stimulated photon emission spectra using a scanning tunnelling microscope. An assignment is made to collective electronic excitations (Mie plasmons) in supported gold clusters which is suggested by model calculations. Plasmon lifetimes, derived from homogeneous line widths, are considerably shorter for gold on Al_2O_3/NiAl (1.8 fs) than for Au/TiO_2 (4.7 fs).

3 CHEMISTRY

3.1 Phase Transfer Synthesis of Novel Water-Soluble Gold Clusters with Tripodal Thioether-Based Ligands

Newly prepared tripodal, water-soluble 1,3,5-trimethylbenzene thioethers have been shown to be suitable ligands for coordination to the $Au_{55}C_{l6}$ cluster. W.M. Pankau, G. von Kiedrowski and K. Verbist, Lehrstuhl für Bioorganische Chemie, Ruhr-Universität-Bochum, Germany, *Chem. Commun. (Cambridge, UK),* 2001, (6), 519-520, evaluated the thioethers for their ability to extract gold into the aqueous phase from a solution of the triphenylphosphine cluster in methylene chloride.

3.2 Synthesis of Luminescent Gold(I) and Gold(III) Complexes with a Triphosphine Ligand

M. Bardaji, A. Laguna, J. Vicente and P.G. Jones of the Departamento de Quimica Inorganica Instituto de Ciencia de Materiales de Aragon, Universidad de Zaragoza-CSIC, Spain, *Inorg. Chem.,* 2001, **40**(12), 2675-2681, have synthesized and characterized trinuclear Au(I) complexes $[(AuX)_3(\mu\text{-triphos})]$ (triphos = bis(2- diphenylphosphinoethyl)phenylphosphine; X = Cl, Br, I, C_6F_5) and di- and trinuclear Au(III) complexes $[\{Au(C_6F_5)_3\}n(\mu\text{-triphos})]$ (n = 2, 3). The luminescence properties of these complexes in the solid state were studied; at low temperature most of them are luminescent, including the Au(III) derivative, with the intensity and the emission maxima being clearly influenced by the nature and the number of the ligands bonded to the Au centres. (see also *Gold Bull.,* 2001, **34**, 14-19 for paper on luminescent gold heteroatom complexes).

4 COATINGS, FILMS, MEMBRANES AND WIRES

4.1 Improved Adhesion of Gold Coatings on Ceramic Substrates by Thermal Treatment

The influence of thermal treatment on the adhesion of thin gold films on alumina ceramic substrates using scratch test measurements has been studied by T.P. Nguyen, J. Ip, P. Le Rendu and A. Lahmar, Laboratoire de Physique Cristalline, Institut des Materiaux Jean Rouxel, Nantes, France, *Surf. Coat. Technol.,* 2001, **141**(1), 108-114. The adhesion was found to be substantially increased when the systems were heat-treated at 500°C, and the adherence depends on the length of treatment. An attempt to explain the improved adhesion was made by XPS. Analysis of the core level spectra of Au, Al, and O recorded in the interfaces showed reactions between Au and Al in both treated and untreated samples. Compared with untreated samples, the interdiffusion of both species at the interface of the treated sample was critically important. In addition, the formation of new compounds was also observed. The improvement in mechanical adherence of the gold thin films on the ceramic substrate is explained by the formation of Au-Al compounds and gold oxide in the interfacial region.

4.2 Thick-Film Gold Conductor Pastes

S. Li of the Kunming Institute of Precious Metals, Kunming, P.R. China, *Guijinshu*, 2001, **22**(1), 57-62, has written a review, with 32 references on thick-film gold conductor pastes. It describes classes of conductor pastes, gold powder, organic carriers and ageing characteristics. Future trends and developments are also considered.

4.3 Preparation of Ultrathin Films Filled with Gold Nanoparticles through Layer-by-Layer Assembly with Polyions

Gold nanoparticles stabilized by a small mercapto-ligand have been assembled using a layer-by-layer alternate adsorption. T. Yonezawa, H. Shimokawa, M. Sutoh, S.-Y. Onoue and T. Kunitake of the Department of Applied Chemistry, Faculty of Engineering, Kyushu University, Fukuoka, Japan, *Stud. Surf. Sci. Catal.,* 2001, **132**(Proceedings of the International Conference on Colloid and Surface Science, 2000), 619-622 have shown that these nanoparticles have high chemical stability, and that sodium chloride could be added to the dispersion to reduce the electrostatic repulsion between the particles. The layers of gold nanoparticles obtained had a golden metallic lustre and electrical conductivity.

5 COLLOIDS AND NANOTECHNOLOGY

5.1 Dendron-Controlled Nucleation and Growth of Gold Nanoparticles

Dendrons that have been focally modified with a metal-coordinating functional group can be utilized as stabilizing media for the controlled growth of gold nanocrystals enclosed by dendrons. R. Wang, J. Yang, Z. Zheng, M.D. Carducci, J. Jiao and S. Seraphin, Department of Chemistry, University of Arizona, Tucson, USA, *Angew. Chem., Int. Ed.,* 2001, **40**(3), 549-552 have shown that with 4-pyridone-based dendrons, gold nanoclusters were obtained that are stable for six months both in solution and in the solid state. The average size of the resulting nanoparticles is a direct function of the generation number of the passivation dendron, with higher generation dendrons producing larger particles.

5.2 Quantitative Evaluation of Electron Beam Writing in Passivated Gold Nanoclusters

A quantitative investigation of direct electron beam writing in monolayer films of passivated gold nanoclusters has been reported by T.R. Bedson, R.E. Palmer, T.E. Jenkins, D.J. Hayton and J.P. Wilcoxon, Nanoscale Physics Research Laboratory, School of Physics and Astronomy, The University of Birmingham, UK, *Appl. Phys. Lett.,* 2001, **78**(13), 1921-1923. In this process, the passivating organic ligands are (partially) removed to create gold-based nanostructures. The fabrication of lines with a width as narrow as 26 nm is reported while measurements of the linewidth as a function of dose allow us to obtain a quantitative measure of the sensitivity, for comparison with established negative tone resists (see also G.M. Francis and R.E. Palmer, *Gold Bull.,* 1996, **29**, 47-51).

5.3 Synthesis of Gold Nanoparticles Dispersed within Pores of Mesoporous Silica Induced by Ultrasonic Irradiation and its Characterization

Gold nanoparticles loaded within pores of mesoporous silica were synthesized *in situ* by sonochemical reduction of chloroauric acid within the pores of silica. W. Chen, W.P. Cai, C.H. Liang and Z.D. Zhang of the Institute of Solid State Physics, Chinese Academy of Sciences, Hefei, Anhui, P.R. China, *Mater. Res. Bull.,* 2001, **36**(1-2), 335-342, carried out the reduction by ultrasonic irradiation in an argon atmosphere at room temperature. The composite was characterized by Brunauer-Emmett-Teller (BET), X-ray diffraction (XRD) and high-resolution transmission electron microscopy (HREM) techniques. It has been shown that nearly spherical-shaped gold nanoparticles, with a fairly narrow size distribution, are isolated from each other and uniformly dispersed within the pores, which are <9 nm in diameter. With the decrease of particle size, a significant red-shift of surface plasma resonance (SPR) band of gold particles was observed in the optical absorption measurement.

5.4 Preparation of Uniform Fluorinated Gold Nanoparticles and Their Highly Ordered Hexagonally Packed Monolayer

T. Yonezawa, S.-Y. Onoue and N. Kimizuka of the Department of Applied Chemistry Faculty of Engineering, Kyushu University, Hakozaki Fukuoka, Japan, *Langmuir,* 2001, **17**(8), 2291-2293, have prepared fluorocarbon-stabilized gold nanoparticles for the first time by the reduction of $AuCl^{4-}$ in the presence of fluorinated alkane thiols as stabilizers. TEM revealed the formation of uniform gold nanoparticles. These fluoro-nanoparticles are soluble only in fluorocarbon media, and casting of these dispersions provided highly ordered, hexagonally packed monolayers on solid substrates.

5.5 The Electrical Properties of Gold Nanoparticle Assemblies Linked by DNA

The electrical conductivity of gold nanoparticles interconnected by DNA have been examined as a function of temperature, oligonucleotide length, and relative humidity by S.-J. Park, A.A. Lazarides, C.A. Mirkin, P.W. Brazis, C.R. Kannewurf, and R.L. Letsinger, Department of Chemistry, Northwestern University, Evanston, IL, USA, *Angew. Chem., Int. Ed.,* 2000, **39**(21), 3845-3848. The DNA-linked nanoparticle structures have been characterized by field emission SEM, synchrotron small angle X-ray scattering experiments, thermal degradation profiles, and UV/Vis spectroscopy.

5.6 Preparation of π-Conjugated Polymer-Protected Gold Nanoparticles in Stable Colloidal Form

Y. Zhou, H. Itoh, T. Uemura, K. Naka and Y. Chujo, Department of Polymer Chemistry, Graduate School of Engineering, Kyoto University, Japan, *Chem. Commun. (Cambridge, UK)*, 2001, (7), 613-614, have shown that π-conjugated polymer-protected gold nanoparticles of narrow size distribution can be prepared in stable colloidal form via reduction of $HAuCl_4$ by a π-conjugated poly(dithiafulvene) having electron-donating properties.

5.7 Atomic Scale Imaging by UHV-AFM of Nanosized Gold Particles on Mica

Gold particles 22 nm in diameter have been grown epitaxially on a muscovite mica support by using atom deposition. S. Ferrero, A. Piednoir and C.R. Henry, CRMC2-CNRS, Marseille, France, *Nano Lett.,* 2001, **1**(5), 227-230, found that the morphology of nanometre-sized gold particles supported on mica can be imaged on an atomic scale *in situ* by using UHV-AFM in contact mode. Top (111) and lateral (100) facets were imaged simultaneously near an edge. On a top (111) facet, an atomic step has been observed.

5.8 Evidence for Seed-Mediated Nucleation in the Chemical Reduction of Gold Salts to Gold Nanoparticles

Central to the concept of seed-mediated growth of nanoparticles is that small nanoparticle seeds serve as nucleation centres to grow nanoparticles to a desired size. This common assumption has been examined in a model system by N.R. Jana, L. Gearheart and C.J. Murphy, Department of Chemistry and Biochemistry Graduate Science Research Center, University of South Carolina, Columbia, USA, *Chem. Mater.,* 2001, **13**(7), 2313-2322. In the wet chemical synthesis of gold nanoparticles via reduction of a gold salt (using TEM and electron absorption spectroscopy) changing the seed concentration does affect the size of the product nanoparticles, but the method of reagent addition drastically affects the outcome even more. For rapid addition of the reducing agent, the presence of seeds appears to promote the formation of more seeds instead of growth. The observed nucleations are drastically enhanced by 99% compared to particle growth. For slow addition of the reducing agent, the seeds do grow, but the product nanoparticle degree of homogeneity in shape is compromised. For higher concentrations of seeds, nanoparticle growth is better controlled for slow addition of reducing agent compared to rapid addition. A mechanistic step to explain the commonly observed size distribution is proposed.

6 ELECTROCHEMISTRY

6.1 Gold Electroplating Solution

A patent has been filed by K. Kitada and Y. Shindo of the Tanaka Kikinzoku Kogyo K.K., Japan, WO Patent 2001027354 A1 (19 April 2001), covering use of a gold electroplating solution consisting of either a gold salt or a gold complex as the gold source, a buffer, an organic gloss agent, and a conductive salt, wherein 1,2-ethanediamine is employed for enhancing the quality of the gold plating and the stability of the electroplating solution.

6.2 Impedance and Morphological Properties of Electroless Gold on Industrial Metal Coupons

An approach for correlating the bath chemistry during electroless gold deposition with the overall plating quality on industrial wire bond samples has been presented by A. Sargent and O.A. Sadik, of the Department of Chemistry, State University of New York at Binghamton, USA, *Langmuir,* 2001, **17**(9), 2760-2767. Electrochemical impedance spectroscopy of the reducing agent dimethylamine borane (DMAB) on gold in alkaline solution was used to provide qualitative information on the interfacial adsorption/desorption processes occurring during deposition.

Depending on hydroxide and DMAB concentration, impedance data obtained under hydrodynamic conditions at the gold oxide reduction potential (0.184 V vs Ag/AgCl) follow two different equivalent circuit models that do not exhibit contributions from diffusion. Gold deposit quality was assessed by SEM and energy-dispersive spectrometry using a variety of bath compositions. The bath efficiency was evaluated in terms of plating rate obtained from x-ray fluorescence data.

The substrate surface/solution interactions are linked to the final quality of the resulting gold layer. Substrate incompatibility and the ratio imbalance between gold and the reducing agent produce thin, dull deposits. Maintaining the optimum ratio of DMAB/KOH provides a balance in the bath chemistry necessary for efficient plating.

6.3 Surface Activation Treatment of Nickel Plating Layer to Improve Adhesion of Gold Plating Layer

This patent describes electrolytic activation of a nickel plating layer with a cyano-containing activator before gold plating takes place (H. Tsuge and H. Yanagida, Matsushita Electric Works, Ltd, Japan, Japanese Patent 2001152351 A2 (5 June 2001). The activator may contain an alkaline electrolytic rust remover and sodium cyanide. The treatment conditions used are 35-70ºC, 7.0 volts and 1.0 s. The treatment improves the adhesion and is useful for wire bonding.

6.4 Novel Cyanide- and Sulfite-Free Gold Deposition

Mercaptoethanesulfonic acid and mercaptopropanesulfonic acid were examined with respect to their Au(I)-complexing behaviour and tested as substitutes for cyanides in galvanic gold separation processes. First results, obtained by F. Simon and W. Kuhn of Degussa Galvanotechnik GmbH, Schwäbisch Gmünd, Germany, *Oberflaechen Polysurf.,* 2001, **42**(1), 10-13, indicate galvanic deposition of fine gold as well as gold alloys in weak alkaline media proceeding sufficiently well. A brief study on hitherto unpublished cyanide- and sulfite-free galvanic systems is included. (see also, Y. Okinaka, *Gold Bull.,* 2000, **33**, 117 - 127).

7 ELECTRONICS

7.1 Manufacture of Glass Ceramics-Based Circuit Boards and the Appropriate Gold-Based Electroconductive Pastes

Glass-ceramic substrates fired at 800-1000ºC are printed with gold pastes containing 0.05-0.2 parts (based on 100 parts Au) Rh and up to 0.5 parts glass frits and fired to form wiring layers with good wire bonding properties (K. Shibata, J. Fukuda, M. Miyairi and K. Naito, Sumitomo Metal Electronics Devices Inc, Japan; Tanaka Noble Metal Industrial Co, Ltd, Japanese Patent 2001135139 A2, 18 May 2001). The frit content in the pastes should be 0.1-1 parts when the substrates are fired under shrinkage restrained conditions. The glass ceramic-based circuit boards manufactured as above show excellent metallizing strength and good appearance.

7.2 Packaging of Circuit Board, Gold-Plating Solution, and Gold Plating

A method for packaging a circuit board involves forming bumps having a number of needle-like protrusions on the terminal surface of a semiconductor device or electrode side of the board by plating, and mounting the semiconductor device on the circuit board to connect the bumps and electrodes (Y. Shindo, Electroplating Engineers of Japan Ltd, Japanese Patent 2001110832 A2, 20 April 2001). A gold plating solution for forming the above bumps contains an Au(III) compound (0.005 - 0.12 mol/L Au ions), a chelating agent of ethylenediamine (0.2 - 2.0 mol/L) or a nitrotriacetate (0.05 - 0.5 mol/L), a conductive salt, a buffering agent, and a stabilizer. Specifically, the stabilizer may be 2,2-bipyridyl, 1,10-phenanthroline, neocuproin, or imidazole. A method for gold plating involves plating in the above gold plating solution at a current density of 0.3-3.0 A/dm^2.

8 MATERIALS SCIENCE

8.1 Gold-Sensitized Silver Halide Emulsion and Colour Photographic Light-Sensitive Material

This patent, filed by S. Yamashita (US Patent 2001003037, 7 June 2001) describes use of an emulsion containing gold-sensitized silver halide grains having a silver chloride content of 95 mol % or more, wherein from 8 to 50% of the gold existing on the silver halide grains is metallic gold. The silver halide emulsion has a high silver chloride content and has high sensitivity and low fogging properties.

8.2 Liquid Gold Compositions for Decorating Fired Inorganic Substrates

The liquid gold consists of a gold lustre compound and 0.05-50% thickening acrylate polymer $[CH_2C(R)C(O)OY]_n$; where R = H or a C_{1-4} alkyl, Y = C_{5-40} hydrocarbyl, which is monocyclic, bicyclic or tricyclic, which may be further carrying substituents. The gold composition, patented by P.A. Marsh, Johnson Matthey plc, UK (WO Patent 2001040392 A1, 7 June 2001), can be used to decorate substrate surfaces and, after firing, forms an excellent, bright film of gold on the decorated substrate surface without black spot formation. An example of such a formulation is Au(SC_6H_4-p-CMe_3) 18.3, poly(isobornyl methacrylate) (mol. wt. 550,000) 40, Rh Et hexanoate solution 4, and xylene 37.7 parts.

8.3 Experimental Investigation on the Thermal Contact Resistance between Gold Coating and Ceramic Substrates

A. Lahmar, T.P. Nguyen, D. Sakami, S. Orain, Y. Scudeller and F. Danes of the Laboratoire de Thermocinetique, École Polytechnique de l'Université de Nantes, UMR CNRS, France, *Thin Solid Films,* 2001, **389**(1,2), 167-172, have demonstrated that there is an important correlation between the thermal contact resistance and the nature of the interfacial domain. This can have an important effect on the performance of thermophysical and mechanical properties of solids in sub-micronic scales. Heat transfer and mechanical properties of gold films deposited on alumina ceramic substrates were directly measured using a photo-thermal method and scratch adhesion tests, respectively. The effect of thickness and thermal treatment on these properties were investigated. Both the morphological change and the formation of a complex in the interface seem to be responsible for the thermal contact resistance and adhesion enhancement in thermally treated samples.

9 MEDICAL AND DENTAL

9.1 Functionalized Gold Electrode for Use as an Impedimetric Immunosensor

An impedimetric immunosensor based on functionalized electropolymerized layers has been developed by O. Ouerghi, A. Senillou, N. Jaffrezic-Renault, C. Martelet, H. Ben Ouada and S. Cosnier, Ingenierie et Fonctionnalisation des Surfaces, École Centrale de Lyon, Ecully, France, *J. Electroanal. Chem.,* 2001, **501**(1-2), 62-69. The proposed experimental procedure involves, primarily, the electrogeneration of an N-substituted polypyrrole, carrying terminal cyano groups, on gold electrodes. The latter was characterized by cyclic voltammetric measurements performed in the range 0-0.8 V. Then, immobilization of the antibodies (anti-rabbit IgG) was achieved through electrostatic interactions between the terminal cyano groups of the polymer and the hydroxyl groups of the antibodies. The efficiency of this immobilization method was revealed by both gravimetric and permeation measurements.

Impedance measurements have been used to characterize the electrical characteristics of the functionalized electrodes in order to optimize the working conditions of the immunosensor. It appears that, at a bias potential of -1.425 V, the Warburg impedance is negligible and the variation of the impedance caused by specific interaction between immune species can be exploited for sensing purposes, especially at low frequency. Thus, the sensor based on this immobilization method exhibits a good selectivity as well as a large linear dynamic range, from 600 ng ml^{-1} to 900 ng ml^{-1}.

10 METALLURGY

10.1 Selectively Coating Solder-Ball and Wire Bond Pads with Gold for Wire Bonding

Solder ball bond pads and wire bond pads may be selectively coated so that the wire bond pads have a thicker gold coating than the solder ball bond pads. In a patent by P. Tandy (US Patent 2001002734, 7 June 2001) it is claimed that this may reduce the embrittlement of solder ball joints while providing a sufficient thickness of gold for the wire bonding process. In general, gold coatings are desirable on electrical contact surfaces to prevent oxidation. However, the optimum thickness of gold which is necessary on solder ball bond pads may vary and excessive gold may be disadvantageous. Thus, by masking the solder ball bond pads during the gold coating of the wire bond pads, a differential gold thickness may be achieved which is the most advantageous for each application.

10.2 Au-Ni-Sn Intermetallic Phase Relations in Eutectic Pb-Sn Solder

Recent work by H.G. Song, J.P. Ahn, A.M. Minor and J.W. Morris, Department of Materials Science and Engineering, University of California at Berkeley, USA, *J. Electron. Mater.,* 2001, **30**(4), 409-414, has shown that an Au-Ni-Sn ternary compound with a nominal composition of $Au_{0.5}Ni_{0.5}Sn_4$ redeposits and grows at the interface between eutectic Pb-Sn solder and Ni/Au metallization during ageing at 150ºC. The present work verifies the existence of the $Au_{0.5}Ni_{0.5}Sn_4$ phase by examining the Sn-rich corner of the Au-Ni-Sn ternary phase diagram. The reconfiguration mechanism of the $AuSn_4$ from the bulk solder is also discussed, with detailed observations of the $Au_{0.5}Ni_{0.5}Sn_4$ microstructure.

The results show that the Ni solubility limit in the $AuSn_4$ phase is *ca* 12 at% at 150ºC, and thus, the $Au_{0.5}Ni_{0.5}Sn_4$ phase is a ternary $AuSn_4$-based compound with high nickel solubility. Due to the slight solubility and the fast diffusion of gold in the eutectic Pb-Sn at 150ºC, the $AuSn_4$ intermetallics in the bulk solder can reconfigure to form an $Au_xNi_{1-x}Sn_4$ compound at the interface where nickel is available. The $Au_xNi_{1-x}Sn_4$ compound layer consists of nanocrystals arranged in a larger grain-like morphology. It appears that the inherent lattice strain of the $Au_xNi_{1-x}Sn_4$ compound and the volume change due to its formation results in a nanocrystalline microstructure.

10.3 Magnetic Resonance-Compatible Aortic Coils from High Gold Content Alloys

This invention concerns high gold content alloys to be used as magnetic resonance-compatible aortic coils and has been filed by G. Ruebben (German Patent DE 29920425 U1, 31 May 2001). The alloy also contains platinum, palladium and other elements.

10.4 Theoretical Prediction of a Phase Transition in Gold

Theoretical investigations on the behaviour of gold under high pressure have been undertaken by R. Ahuja, S. Rekhi and B. Johansson, Department of Physics, Condensed Matter Theory Group, Uppsala University, Sweden, *Phys. Rev. B: Condens. Matter Mater. Phys.,* 2001, **63**(21), 212101/1-212101/3. Using first principles of self-consistent total-energy calculations within the local-density approximation as well as generalized gradient approximation and the full-potential muffin-tin-orbital method they found a phase transition from fcc-type to hcp-type of structure at 241 GPa. The stability of this phase has been explained using the electronic density of states.

10.5 Experimental Observations of Dislocation Core Structures in Gold and Iridium

The ability to develop atomic level models of dislocation core structures that are based on first-principles or atomistic calculations has increased significantly in recent years, and in many ways these theoretical models have outpaced experimental observations. An HREM study was undertaken by T.J. Balk and K.J. Hemker, Departments of Mechanical Engineering and Materials Science and Engineering, The Johns Hopkins University, Baltimore, MD, USA, *Mater. Sci. Eng., A,* 2001, **A309-310**, 108-112, to provide an experimental benchmark for such models. *In-situ* TEM observations were used to identify the presence of screw and 60 degree dislocations, and HREM images of these dislocations in both gold and iridium were recorded.

Computer-based image analysis was employed to characterize subtle in-plane atomic level displacements, and direct comparisons with image simulations were used to measure the separation distance between dissociated Shockley partial dislocations. The separations measured were in good agreement with recently obtained theoretical predictions based on the first-principles calculations of Mryasov and Freeman.

11 REFINING

11.1 Lead-Catalysed Gold Dissolution

Gold may be leached from its ores using the well established MacArthur-Forrest method, but to date there has been little agreement on the underlying kinetics and mechanism of the process. M.I. Jeffrey and I.M. Ritchie, *J. Electrochem. Soc.,* 2001, **148**, D29, have now found that when ultrapure reagents are used, the reaction is immeasurably slow. When the reaction is, however, conducted using solutions prepared from analytical-grade reagents containing ppb levels of lead or other impurities, gold leaches much faster. The variations in reported reaction rates are assigned to variations in impurity levels: the presence of lead is thought to accelerate dissolution of a chain-like film of AuCN and this is the rate-limiting step.

11.2 The Application of Ore Immobilization to the Bioleaching of Refractory Gold Concentrate

A new type of bioreactor is proposed for the biological oxidation of refractory gold ores. D. Karamanev, A. Margaritis and N. Chong, Department of Chemical and Biochemical Engineering, The University of Western Ontario, London, Canada, *Int. J. Miner. Process.,* 2001, **62**(1-4), 231-241, have shown that in order to reduce the intraparticle friction, to reduce the energy consumption and increase the volumetric rate of oxygen transfer, the sulfide particles may be entrapped into the pores of an inert material (non-woven textile). This immobilized ore bioreactor can handle up to 40% w/v of pyrite, which is twice the typical value for classic slurry bioreactors. The volumetric rate of pyrite oxidation by *thiobacillus ferrooxidans* in the new reactor was 2.5 times higher than that in a slurry bioreactor operating under similar initial conditions.

11.3 Ammoniacal Thiosulfate Leaching of Ovacik Gold Ore

Thiosulfate leaching of precious metals has been developed as an alternative and nontoxic technique to conventional cyanidation. The aim of this work, decribed by F. Arslan and B. Sayiner, Mining Faculty, Mineral and Coal Processing Section, Istanbul Technical University, Turkey, *Miner. Process. 21st Century, Proc. Int. Miner. Process. Symp., 8th,* 2000, 517-522, ed. G. Ozbayoglu, published by A.A. Balkema, Rotterdam, The Netherlands, was to investigate the possibility of leaching gold and silver into ammoniacal thiosulfate solutions on a laboratory scale.

Samples used in the experiments were taken from Ovacik gold ore deposit, Bergama, Turkey. The influence of temperature and copper sulfate, ammonia, thiosulfate and sodium sulfite concentrations and solid/liquid ratio on gold and silver leaching recoveries were investigated and optimum leaching conditions determined. Under these conditions almost 100% gold and silver leaching recoveries were achieved.

11.4 Are There Realistic Alternatives to Cyanide as a Lixivant for Gold

This review by I.M. Ritchie, M.J. Nicol and W.P. Staunton, A J Parker Cooperative Research Centre for Hydrometallurgy, Perth, Australia, 'Cyanide: Social, Industrial and Economic Aspects', *Proc. Symp. Annu. Meet. TMS,* 2001, 427-440, ed. C.A.Young, L.G. Twidwell and C.G. Anderson, Publisher: Minerals, Metals & Materials Society, Warrendale, Pa, describes how cyanide owes its great success as a lixivant for gold to the great strength of the Au-CN- bond. A replacement for cyanide must similarly be a strong complexing agent for gold (I) or gold (III). The various alternatives are briefly considered and it is concluded that only thiosulfate has a reasonable chance of replacing cyanide as a relatively non-toxic lixivant at the present time. However, there are considerable technical problems to be overcome before thiosulfate can be considered to be a realistic alternative to cyanide. Firstly, the leaching of gold using aerated ammoniacal thiosulfate with copper as a catalyst is a complex process which needs to be understood and controlled carefully in order to achieve maximum recoveries with minimum reagent losses. Secondly, there needs to be an option similar to the CIP process for recovering and concentrating the dissolved gold thiosulfate complex from the pulps produced in the processing of low grade gold ores. The prospects for overcoming these technical challenges are evaluated and discussed.